8-1-1975

The Relationship Between Pulse Rate and Speed as a Measurement of Performance for Competitive Swimmers

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THE EFFECT OF TEMPERATURE AND PRESSURE ON THE SORPTION ISOTHERMS OF DAKOTA LIGNITE

by

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A thesis submitted to the College of Engineering of the University of North Dakota in Partial fulfillment for the degree of Master of Science in Chemical Engineering.

March 24, 1932 Grand Forks, North Dakota

This thesis, presented by Moses Gordon as a partial fulfillment of the requirements for the degree of Master of Science in the University of North Dakota, is hereby approved by the Committee in charge of his work.

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Introduction.

The industrial development of this country has been due largely to the abundant supply of coal within its borders. During this very rapid development, however, little attention has been paid to the matter of coal supply with the result that our largest production has been from the high rank coal fields. When it is realized that these fields represent the smallest quantity of the coal supply it becomes apparent that attention must turn ultimately to the lower rank coals which represent, by far, the largest reserve.

The economic utilization of lignite and sub-bituminous coal must, therefore, become a problem of concern to those connected with the fuel industry. Whereas, in the utilization of high rank fuels the problem is one of efficiency in mining and combustion, in the case of the low rank coals, the problem is primarily that of beneficiation.

It was early realized that the high water content of this fuel renders some form of dehydration necessary. Obviously, the first logical step in the development of any process for the successful dehydration of lignite must be the study of the fundamental characteristics of the moisture in this fuel. One feature of this study has been the determination of the aqueous tension of the moisture in lignite (7). The results of this early study seemed so important that it was decided to continue the work both at higher temperatures as well as with processed lignites. This thesis deals with the results of this extended study.

Previous investigators (6, 7, 9, 11, 12) have called attention to the similarity of wood and coal sorption isotherms. It was thought advisable to study the isotherms of woods occurring in this region. The results are given in this thesis.

Experimental Methods.

The sorption of a vapor by a solid adsorbent may be studied either in the absence or presence of some foreign gas such as air. If carried out in the presence of air, the studies follow either; (1) a dynamic or streaming method; or (2) a static or desiccator method. Lavine and Gauger (7) adopted the desiccator method for the work with lignite primarily because this method was rapid and gave results that were applicable to industrial use. Seborg and Stamm (13) have reached a similar conclusion in adopting a streaming method for studying the sorption of water vapor by paper making materials. It is reasonable to assume that a steady state is attained in either method.

The procedure used in the present investigation was essentially that adopted by Lavine and Gauger (7) and, described briefly, consisted as follows:

The samples of lignite were crushed, ground and sized to 80-100 mesh as rapidly as possible to minimize air-drying losses. Samples of approximately one gram each were weighed into small weighing bottles and placed in desiccators in which the humidity was controlled by means of certain saturated salt solutions and sulphuric acid solutions of known vapor pressures. The samples were weighed from time to time until successive readings varied

by no more than 0.5 mg. The process was repeated with these samples placed in desiccators over concentrated sulphuric acid whereby dehydration at zero vapor pressure was completed. The completely dehydrated samples were then replaced in their original desiccators to obtain the hydration curves.

A list of the solutions used to maintain the required humidities at 20° C. and 50° C. is given in Table 1.

Table 1.

Vapor Pressure Data of Sulfuric Acid and Saturated Salt Solutions Used to Maintain Constant Humidities.

Desiccating Agent	Relative Humidity at 20° C.	Relative Humidity at 30° C.
K_2SO_4	98.5	95.8
$Pb(NO_3)_2$	98.0	----
KCl	85.0	80.0
KBr	84.0	----
NaCl	76.0	74.1
NH_4NO_3	67.0	46.4
$NaNO_3$	----	67.3
KNO_2	45.0	----
H_2SO_4(Sp.gr.= 1.310)	55.4	----
H_2SO_4(Sp.gr.= 1.325)	52.0	----
H_2SO_4(Sp.gr.= 1.400)	33.5	----
H_2SO_4(Sp.gr.= 1.402)	33.2	----
H_2SO_4(Sp.gr.= 1.461)	22.1	----
H_2SO_4(Sp.gr.= 1.478)	19.2	----
H_2SO_4(Sp.gr.= 1.537)	11.3	----
H_2SO_4(Sp.gr.= 1.385)	----	37.1
H_2SO_4(Sp.gr.= 1.433)	----	28.5
H_2SO_4(Sp.gr.= 1.484)	----	19.7
H_2SO_4(Sp.gr.= 1.576)	----	7.2
H_2SO_4 (Sp.gr.= 1.667)	----	2.3

Concerning the Samples Used.

The samples used in this research were obtained from the following sources:

1. Studies at 50° C. -- The samples were received in sealed mason jars from the Truax-Traer Coal Company, Kincaid, North Dakota and from the Miller Coal Company, Burlington, North Dakota. The analyses of these samples on the "as-received" basis are as follows:

	Kincaid %	Burlington %
Moisture	36.2	36.5
Volatile matter	26.3	24.9
Fixed carbon	31.6	31.6
Ash	5.9	7.0
Sulfur	0.2	0.2
B.t.u. per lb.	6,982	6,584

2. Studies at 20°C. with Steam Dried Lignite. -- The samples were obtained from the investigation of Lavine, Gauger and Mann (8) in which Dakota lignite was dried with saturated steam at elevated pressures. These samples were air-dried immediately after being processed and then pulverized and placed in well stoppered bottles until needed. Data for these samples chosen for the sorption experiments are given as follows:

Sample No.	16	19	17	7	26	32	34
Mine	Lehigh	Velva	Velva	Velva	Garrison	Velva	Velva
Original moisture content, %	41.21	36.69	34.86	35.49	34.35	36.73	35.00
Moisture content-air dried basis, %	17.11	13.88	13.46	13.72	10.00	8.56	9.28
Moisture content at time of work, %	10.98	10.88	9.75	9.52	10.68	7.56	8.95
Steam pressure used - atmospheres	5.0	7.0	9.0	10.50	13.00	13.00	15.00

Data and Results.

The Rate of Loss of Moisture from Lignite at 50° C. Lavine and Gauger (7) found that the time required to attain equilibrium at 20° C. by the desiccator method was about 40 days. At a temperature of 50° C. it was found by the present writer that the time was shortened to approximately eight days, due probably, to the increased rate of diffusion of the moisture. Figure 1 represents graphically the rate of loss of moisture at 20° C. and 50° C. from a sample of freshly mined lignite of 80-100 mesh when placed over concentrated sulphuric acid. Data for the 50° C. curve is tabulated in Table 2.

Table 2.

Rate of Loss of Moisture at 50° C.

Days	Total weight	Moisture loss (%)
0	17.2554	0.0
2	16.8790	37.43
4	16.8786	37.47
7	16.8781	37.52
9	16.8781	37.52
13	16.8781	37.52

Vapor Pressure of the Moisture in Lignite at 50° C. The results of the experiments showing the effect of dehydration and subsequent hydration on the vapor pressure at 50° C. of the moisture in two samples of Dakota lignite are tabulated in Table 3. The average results are plotted in Figure 2.

A consideration of Figure 2 shows that the vapor pressure decreases as the moisture content is reduced and also that hysteresis is present at this higher temperature. When these results are

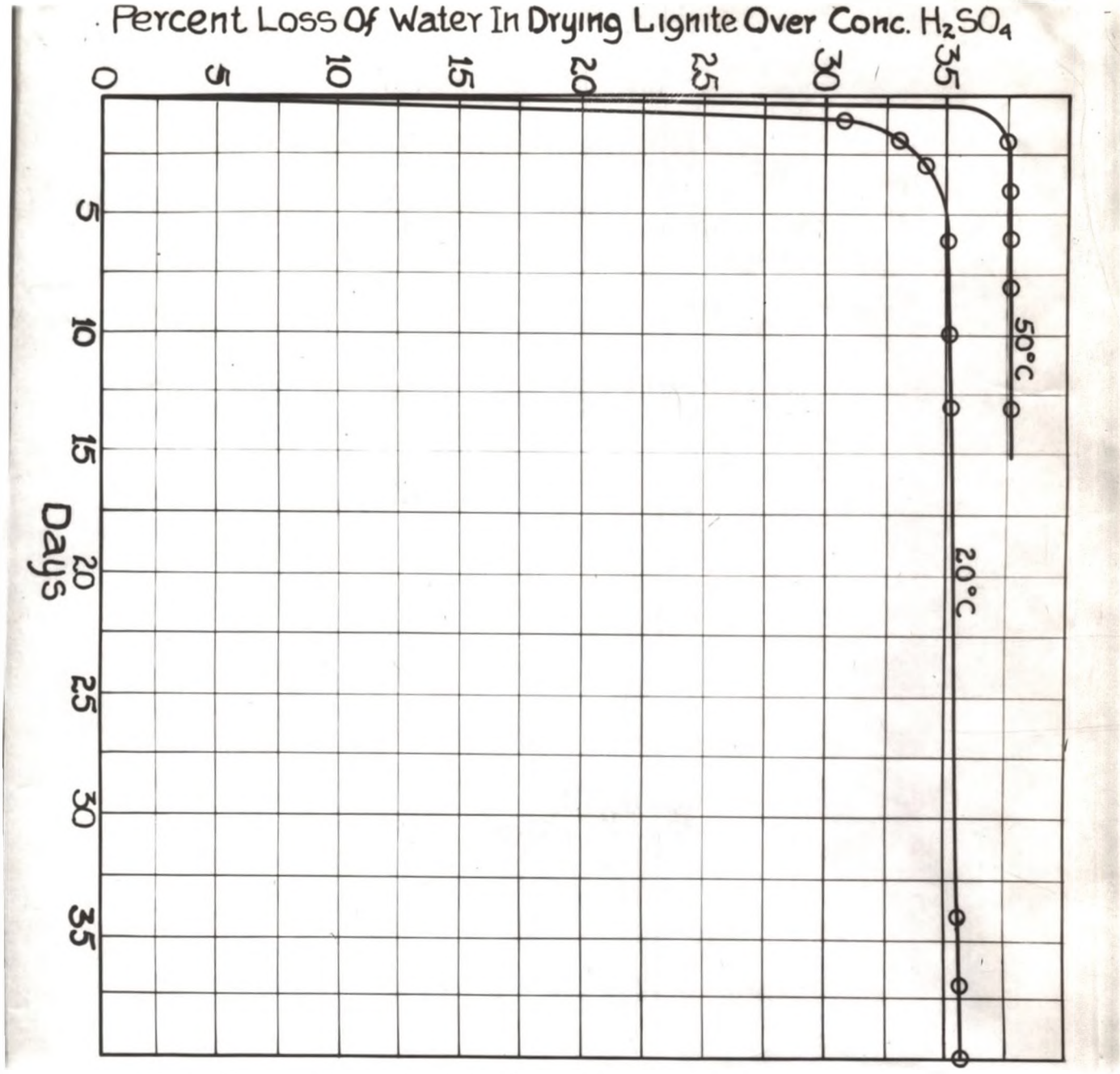

FIG. 1.— RATE OF LOSS OF MOISTURE OVER CONC. H_2SO_4 AT 20°C AND AT 50°C.

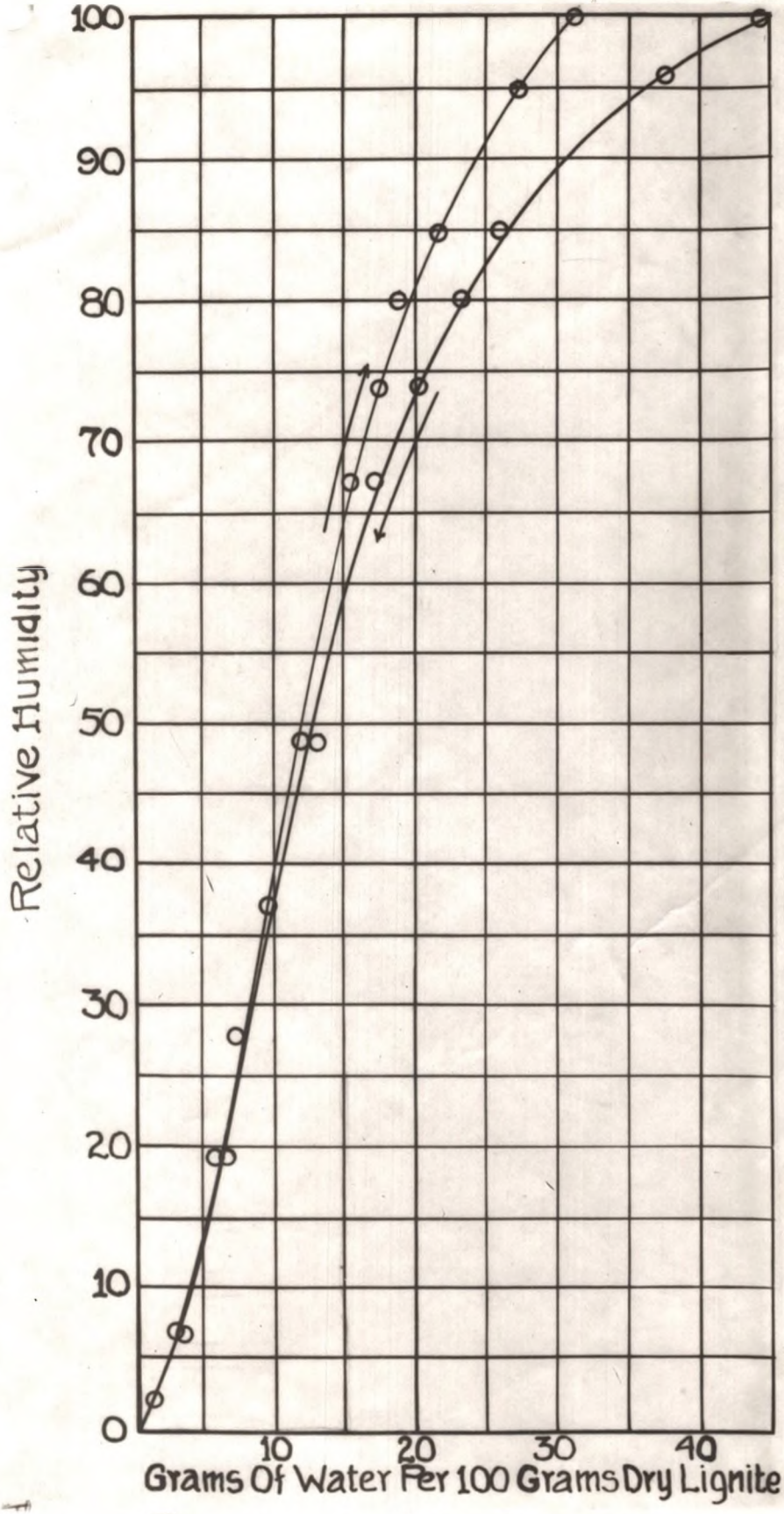

FIG. 2.— 50°C VAPOR PRESSURE ISOTHERMS FOR LIGNITE

compared with the results of the earlier study at lower temperatures it is found that the characteristics of the sorption curves are essentially similar. However, the region of hysteresis is decidedly smaller at 50° C. and this indicates that the increase in temperature has altered the physical structure of the lignite. Further reference to this phenomenon will be made later in this paper.

Table 3.

Vapor Pressure-Moisture Equilibrium Data at 50° C.

Desiccator	Relative Humidity	Moisture - Dry Basis					
		DEHYDRATION			HYDRATION		
		Kincaid	Miller	Average	Kincaid	Miller	Average
	%	%	%	%	%	%	%
1	100.0	48.27	40.75	44.51	30.58	31.82	31.20
2	95.8	30.46	35.74	37.60	27.64	27.56	27.60
3	85.0	26.05	25. 8	25.76	21.25	21.69	21.47
4	80.0	23.20	23.45	23.31	18.43	19.34	18.88
5	74.1	19.39	20.97	20.18	17.08	17.46	17.27
6	67.3	17.08	16.97	17.02	15.44	15.65	15.55
7	48.4	12.91	12.67	12.79	12.17	12.23	12.20
8	37.2	9.65	9.26	9.45	9.43	9.49	9.46
9	28.3	7.02	7.47	7.24	6.10	7.39	6.75
10	19.7	6.01	6.03	6.02	5.85	4.85	5.34
11	7.2	3.19	3.24	3.21	3.18	3.13	3.15
12	2.3	1.53	1.74	1.63	1.44	1.65	1.54

Vapor Pressure of the Moisture in Steam Dried Lignite.--Mention has been made already that the samples chosen for this study were obtained from the work of Lavine, Sauger and Mann (8). These investigators found that lignite dried by this method retains its

physical lump form very well. A consideration of their data led them to conclude that steam drying produces a material change in the colloidal structure of the fuel. Thus, it was found that a sample of steam-dried lignite will dry to a much lower moisture content than will a corresponding sample of freshly mined lignite when both are subjected to identical air-drying conditions. Data showing this effect are given in Table 4. Representative samples of the steam-dried and the corresponding freshly mined lignite were air-dried for 24 hours and moisture determinations were made then by the standard method.

This phenomenon was of sufficient interest to warrant further study. It was decided, therefore, to determine the nature of the sorption process for the system processed lignite-water vapor. However, it was realized that the air-drying of the processed lignite samples might in itself influence the sorption process. It was decided, therefore, to study a sample of freshly mined lignite that was first air-dried.

Table 4.

Moisture Analyses of Raw and Steam-Dried Lignite
(Air-dried basis)
Lavine, Gauger and Mann (8).

Experiment No.	Freshly mined %	Steam-dried %
14	21.36	14.90
17	21.55	13.48
20	22.19	12.80
24	16.68	10.39
27	21.29	12.13
30	19.85	15.58
32	15.02	8.56
33	20.35	10.95
34	21.01	9.28

Data concerning the steam processed samples have been given above. The samples were studied simultaneously with a sample of freshly mined Velva lignite that was first air-dried to a moisture content of 15.02 per cent and which will be referred to as sample No. 34 wet. A portion of this freshly mined lignite was steam-dried and a sample of the product was then air-dried simultaneously with the sample of freshly mined material and is referred to in the tables to follow as sample No. 34 dry.

The sorption studies with these materials were conducted at 20° C. by the method described. The results for two series of experiments are tabulated in Tables 5 and 6. Some of these results are plotted in Figure 3.

A consideration of the curves shown in Figure 3 reveals an interesting phenomenon, namely, that hysteresis has been practically eliminated in the case of steam dried lignite. The accuracy of the desiccator method does not warrant the statement that hysteresis is eliminated entirely since some discrepancy was found in the regions of very low moisture contents. However, it is the opinion of the writer that this discrepancy is due mainly to the method rather than the material. For all practical purposes the present study indicates a complete reversibility.

The sorption curves for lignite processed at pressures of 7.0, 9.0, 10.5 and 15.0 atmospheres are found to be practically identical. This indicates that the effect of pressure as related to the sorption process is constant through this range.

Table 5.

Sorption Data for Steam-Dried Lignite, Series A.

Relative Humidity 30° C. %	MOISTURE - DRY BASIS									
	#26 %		#32 %		#34 dry %		Average %		#34 wet %	
	A	B	A	B	A	B	A	B	A	B
98.0	28.26	31.08[a]	28.94	31.08[a]	27.47	31.11[a]	28.25	31.09[a]	36.25	36.05[a]
84.0	19.32	19.97	19.91	20.16	19.08	19.96	19.43	20.03	27.06	22.50
76.0	17.87	17.94	18.26	18.28	17.64	17.81	17.92	18.01	25.79	20.51
67.0	15.32	15.85	15.80	15.88	15.15	15.22	15.42	15.42	18.56	14.99
55.4	13.57	13.46	13.71	13.66	13.54	13.52	13.61	13.55	18.29	14.86
45.0	11.89	11.66	11.80	11.84	11.96	11.78	11.88	11.76	15.22	13.80
33.2	10.63	9.65	10.50	9.76	10.79	9.90	10.64	9.81	11.93	10.52
19.2	8.41	7.31	8.33	7.34	8.52	7.29	8.42	7.31	8.55	7.54
11.3	6.13	5.25	6.13	5.29	6.23	5.34	6.16	5.29	6.59	5.99

Data concerning above coals.

Mine	Garrison	Velva	Velva	- - - -	Velva
Processing Pressure Atmosphere	13	13	15	- - - -	unprocessed
Moisture at end of Processing %	15.59	16.95	13.10	- - - -	- - - -
Moisture of samples used in the sorption experiments	10.68	7.56	8.95	- - - -	16.02

[a] Relative humidity for these samples is 98.5%.

A = Dehydration values.

B = Hydration values.

Table 6.
Sorption Data for Steam-Dried Lignite, Series B.

Relative Humidity 30° C. %	MOISTURE - DRY BASIS									
	#16 %		#19 %		#17 %		#7 %		#34 %	
	A	B	A	B	A	B	A	B	A	B
98.5	31.60	-----	28.40	-----	29.26	-----	28.05	-----	28.70	-----
92.0	26.61	27.19	24.14	24.15	24.59	24.45	23.60	23.91	24.14	24.59
85.0	22.24	22.71	20.09	20.72	22.17	20.83	19.46	20.00	20.18	20.44
76.0	17.82	18.54	17.51	17.39	18.56	17.61	16.86	17.08	17.00	17.08
67.0	16.87	16.86	13.68	13.68	15.01	13.42	14.69	14.80	14.56	14.65
52.0	15.06	13.70	13.57	12.44	13.07	12.35	12.85	12.03	12.28	11.87
45.0	14.20	13.32	13.07	12.23	12.42	12.20	12.16	11.76	11.44	11.49
33.0	12.60	10.42	11.28	9.34	11.14	9.42	10.71	9.31	10.01	9.18
22.0	9.15	7.88	8.00	7.40	8.43	7.78	8.88	7.83	7.72	7.35
11.0	6.85	5.82	6.28	5.36	6.39	5.45	5.90	5.20	5.73	5.01

Data concerning above coals.

Mine	Lehigh	Valva	Valva	Valva	Valva
Processing Pressure Atmosphere	%.) 5.0	7.0	9.0	10.5	15.0
Moisture at end of Processing %	30.52	22.72	19.21	21.14	13.10
Moisture of samples used in the sorption experiments	10.98	10.88	9.75	9.52	8.95

A = Dehydration values.

B = Hydration values.

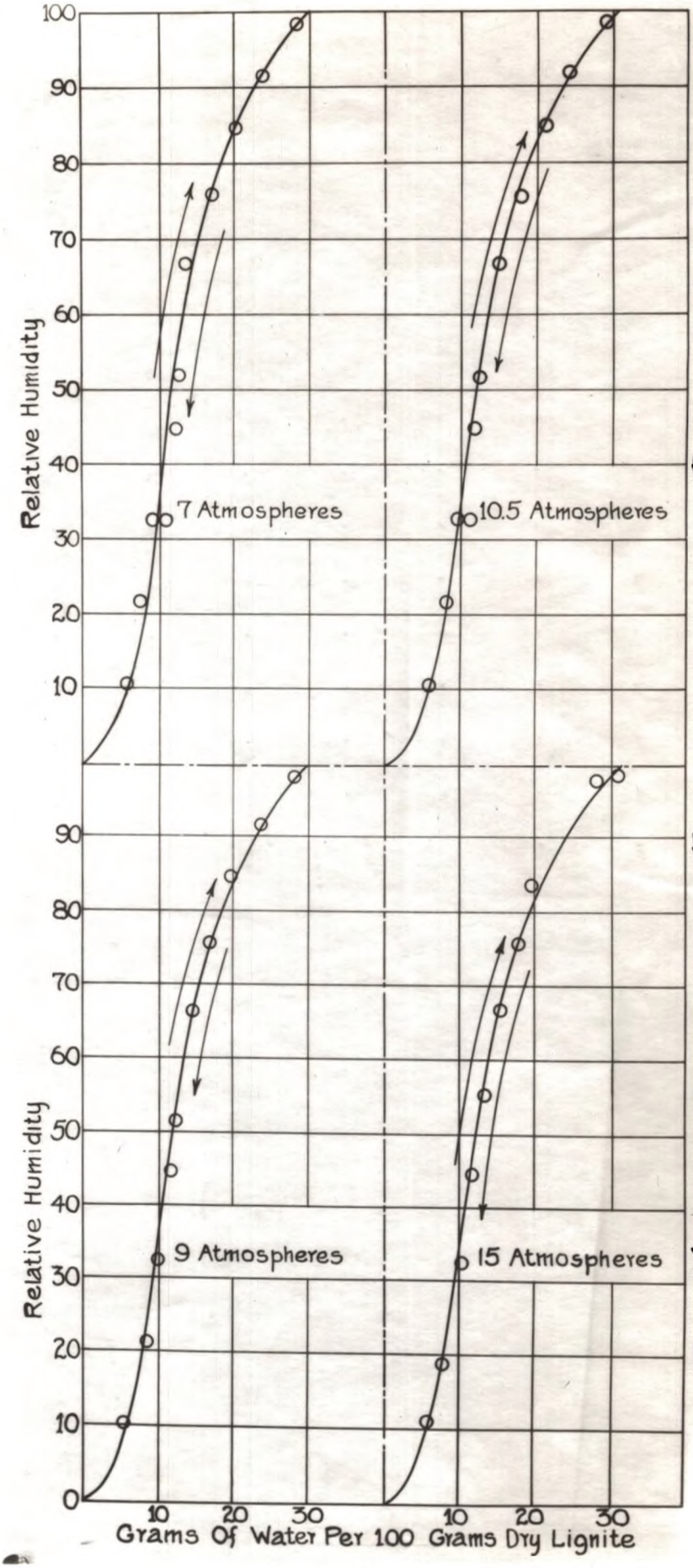

FIG. 3 — VAPOR PRESSURE ISOTHERMS FOR PROCESSED LIGNITE (20°C)

The Effect of Air-Drying on the Nature of the Sorption Process.

The effect of a lowered moisture content on the nature of the sorption process can be seen from Figure 4 in which are plotted sorption data at 20° C. for : (1) a sample of freshly mined Velva lignite; (2) a sample of air-dried Velva lignite; and (3) a sample of air-dried processed Velva lignite. The data for the freshly mined sample was obtained from the work of Lavine and Gauger (7). Emphasis is again made to the fact that samples 2 and 3 as above were air-dried simultaneously.

A consideration of this Figure (4) shows very clearly that air drying does not alter materially the nature of the sorption process. Hysteresis is very marked in the case of the air-dried sample. A direct comparison cannot be made since these samples were not obtained simultaneously although they were obtained f rom the same mine. It is evident, however, that the air-drying of the steam processed sample cannot account for the elimination of hysteresis with this material.

The Vapor Pressure of Wood at 20° C.

The following samples were used in this experiment obtained through courtesy of Dr. Raphael Zon:

(1) Tamarack. Section from a point about 3 feet from the ground. Collected from a tamarack swamp about 1 mile east of Dorsey, Alger County, Michigan on December 4, 1930.

(2) Black Spruce. Section from a point 3 to 4 feet above the ground. Collected from the same swamp as the tamarack.

(3) Northern white cedar. Section from a point 3-4 feet from the ground. Collected from the same swamp as the other two.

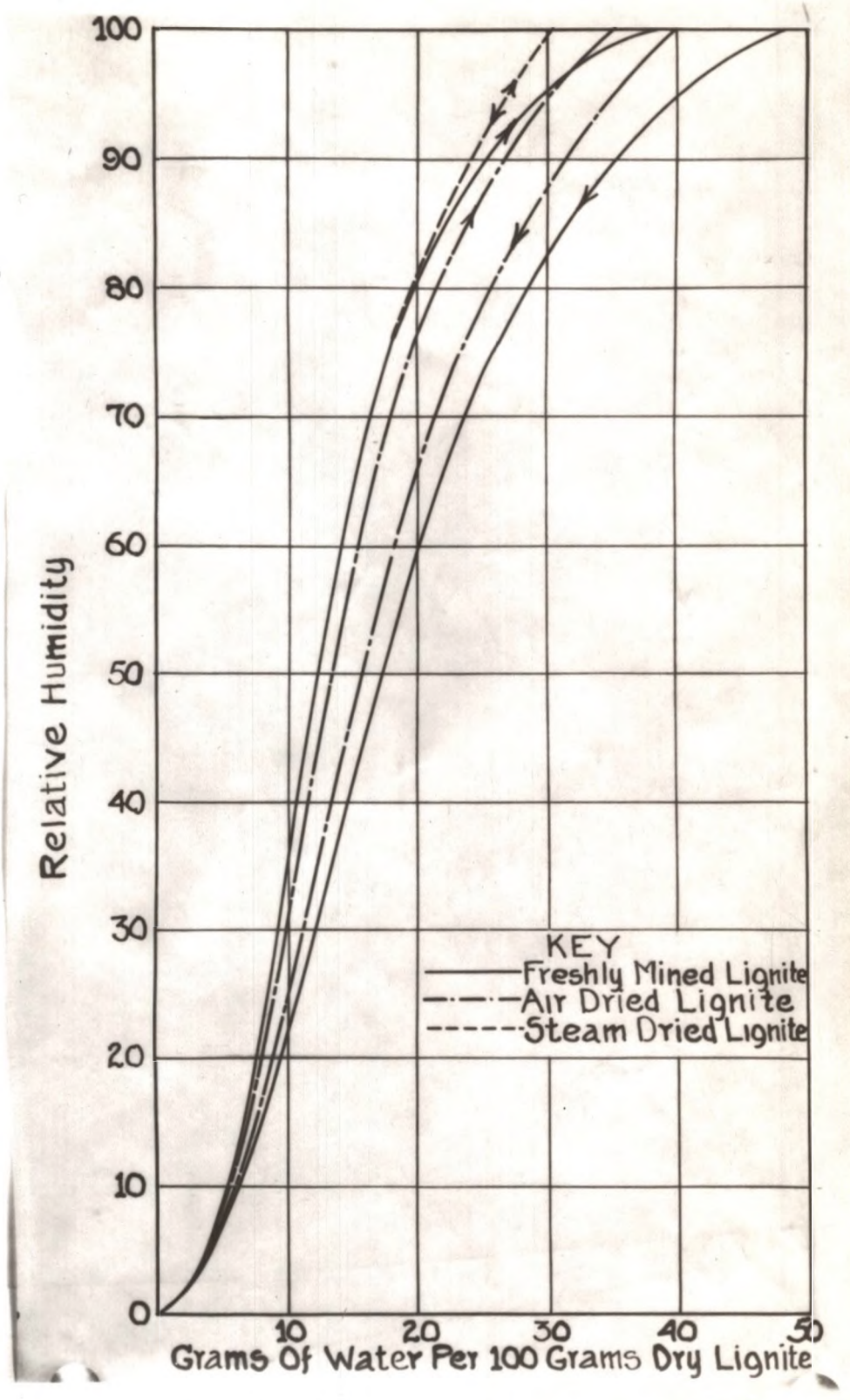

FIG. 4. VAPOR PRESSURE ISOTHERMS AT 20°C.

The procedure followed was the same as that with lignite. Thin shavings of the sapwood were used. Pidgeon and Maass (11) have shown that there is no difference between the vapor pressure of sapwood and of heartwood.

Table 7 gives the results obtained for the three woods. The isotherms are plotted in Figure 5.

Table 7.

VAPOR PRESSURE-MOISTURE EQUILIBRIUM DATA OF WOOD AT 30° C.

Desi	R.H.	Moisture - Dry Basis: Dehydration: Tamarack	Dehydration: Spruce	Dehydration: Cedar	Dehydration: Average	Hydration: Tamarack	Hydration: Spruce	Hydration: Cedar	Hydration: Average
1	98	33.84	38.22	------	35.03	28.90	29.30	29.50	29.20
2	92	33.52	29.29	32.79	31.87	27.51	24.08	25.23	25.60
3	84	22.40	21.51	22.39	22.10	17.55	16.98	17.39	17.24
4	76	19.77	18.80	19.18	19.25	14.50	14.30	14.10	14.30
5	67	14.71	15.40	15.12	15.08	12.48	12.52	12.38	12.46
6	52.	12.00	12.17	11.98	12.05	10.69	10.88	10.72	10.76
8	33.2	9.01	8.21	8.05	8.42	7.53	6.65	6.56	6.85
9	22.1	6.76	6.99	6.86	6.87	5.45	5.18	5.34	5.32
10	11.5	4.09	4.38	4.14	4.20	3.31	3.39	3.19	3.30

General Considerations.

The Effect of Temperature on the Sorption Process.

The effect of temperature is seen from Figure 6 in which are plotted sorption data for lignite - water vapor at temperatures of 30° C., 40° C., and 50° C., and also the sorption data at 30° C. for steam processed lignite. In general, it is found that the characteristics of the sorption curves are similar in many respects. However, it is seen that the region of hysteresis is reduced as the temperature is increased from 30° C. The included hysteresis areas were measured by a planimeter and the following values obtained:

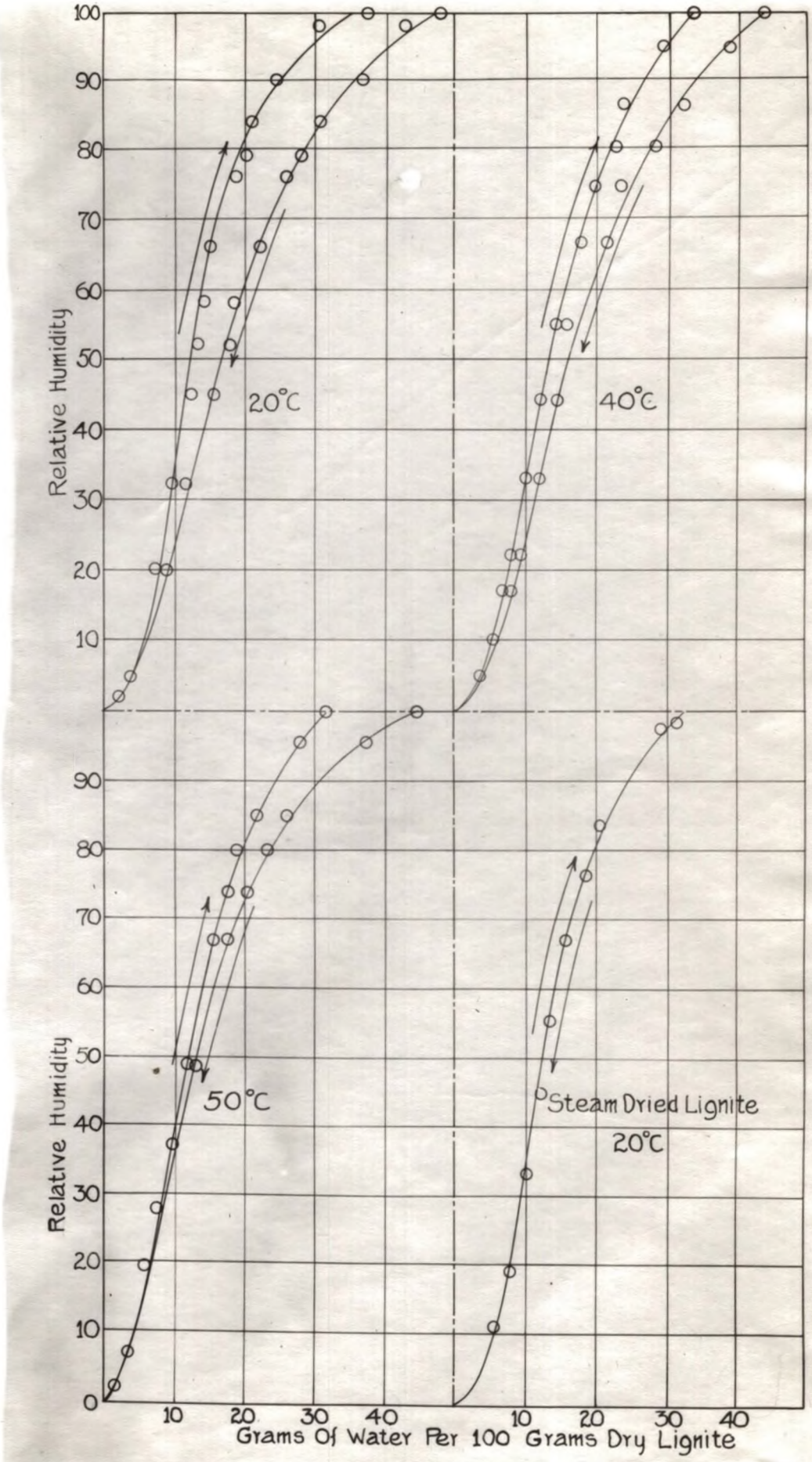

FIG. 6.- EFFECT OF TEMPERATURE ON THE SORPTION CURVES FOR LIGNITE.

Temperature °C.	Hysteresis Area (cm^2)
20	34.31
40	20.12
50	14.25
20 (steam dried lignite)	00.00

Hysteresis.

Several theories have been advanced to explain this general phenomenon. They fall under the following headings:

(1) Difficulty of wetting. Zsigmondy (16) states that once the capillary walls have been dried, they are wetted with difficulty during hydration. The moisture has been replaced by the gases of the air, chiefly oxygen. The meniscus of the capillary is therefore less concave, the radius of curvature greater and the vapor pressure is greater for the same moisture content. Anderson (3) showed that under vacuum the region of hysteresis is decreased but little. Allmand and his co-workers (1) have found hysteresis in the moisture isotherms of activated charcoal. Zsigmondy's explanation, while no doubt in part correct, is incomplete.

(2) Rate of attainment of equilibrium. Patrick and Opdyke (10) make the statement that the region of hysteresis will disappear in silica gel if enough time be given to reach equilibrium. Porter and Ralston (12) also suggest that hysteresis may be due to the slow rate at which coal takes up moisture when its vapor pressure is almost equal to that of the atmosphere surrounding it, "making it possible that in the experiments complete equilibrium is not attained." The experiments of Lavine and Gauger (7) and the writer (Table 8 and Figure 1) seem to indicate that with lignite

the explanation is not correct.

(3) The presence of inorganic materials. Coolidge (3) attributes hysteresis in charcoal largely to the preferential adsorption of moisture by inorganic materials. Work presented in this paper has shown Coolidge's theory to be incorrect for lignite. Tables 5 and 6 shows that in lignite processed at 13-15 atmospheres hysteresis has been eliminated to a great extent. This would not be the case if non-reversibility were due to the presence of ash.

Experiments conducted on vapor pressure on Dakota lignite indicate that shrinkage is the fundamental cause for hysteresis. With determinations at room or slightly elevated temperatures, the hydrogel does not set during dehydration; hence, there is a modification in structure during dehydration and hydration that does not permit the two to be reversible.

When lignite is heated in an atmosphere of saturated steam at about 190° C. (13 atmospheres) the structure is definitely modified and the gel set so that vapor pressure determinations conducted at room temperature show almost complete reversibility. The slight hysteresis evidenced at lower humidities (see Tables 5 and 6) indicates that occluded gases do to some extent prevent reversibility. This supports Zsigmondy's view on the difficulty of wetting dried capillaries.

Pore Size.

From a purely thermodynamic basis it is possible to calculate the pore size of lignite and wood from the vapor pressure isotherms. This is done by the application of the well known Thompson Equation (15):

$$r_c = \frac{2\sigma M}{\rho RT \ln \frac{P}{P_c}}$$

r_c = radius of capillary

σ = surface tension of water

M = molecular weight of water

ρ = density of water

R = gas constant

T = temperature, degrees Kelvin

P = vapor pressure from a plane surface

P_c = vapor pressure from capillary water

The results of such calculations are listed in Table 7 and are plotted in Figure 7.

For example, let us take a capillary at 20° C. in which the water is in equilibrium with an atmosphere in which the relative humidity is 90%.

$$r_c = \frac{2 \times 72.75 \times 18.02}{0.9983 \times 8.316 \times 10^{-7} \times 293 \times \ln \frac{100}{90}}$$

whence,

$$r_c = 10.31 \times 10^{-7} \text{ cm.}$$

Columns 1 and 2 in Table 7 give the results obtained for radii as a function of the relative humidities.

To calculate the fraction of water bound within any given limits of pore size we may employ the expression

$$\frac{T-E}{T}$$

where T and E are the amounts of moisture in equilibrium with the atmosphere at the relative humidities in question. It is desired to compare the moisture distribution in the smaller pores so that in all cases T is the value at a relative humidity of 100% while

E is the moisture content for each humidity lower than 100%. For example to obtain the value of 38.50% in column 3, Table 7, it is merely necessary to go to the 20° isotherm for lignite and get the values T and E at 100% and at 90% respectively.

$$\frac{T-E}{T} = \frac{54.0 - 33.2}{54.0} = .385$$

From this we deduce that 38.5 per cent of the moisture (00% saturation pressure) is held in capillaries whose radii are less than 10.31×10^{-7} cm.

(Values for lignite at 20° C. taken from the work of Larian (6)).

Table 7.
Moisture Held Within Various Pore Radii Intervals.

Relative Humidity	Lignite at 20°C Radius cmx10^{-7}	Lignite at 20°C Per cent[a]	Lignite at 40°C Radius cmx10^{-7}	Lignite at 40°C Per cent[a]	Lignite at 50°C Radius cmx10^{-7}	Lignite at 50°C Per cent[a]	Steam-dried lignite Radius cmx10^{-7}	Steam-dried lignite Per cent[a]
90.0	10.31	38.50	9.28	22.73	8.83	31.11	10.31	24.26
84.0	6.20	44.34	5.58	32.05	5.31	42.22	6.20	34.10
76.0	3.93	49.36	3.54	42.05	3.36	53.33	3.93	42.95
66.0	2.60	54.05	2.34	52.27	2.23	63.11	2.60	49.83
52.0	1.65	61.75	1.48	62.07	1.41	71.33	1.65	57.70
45.0	1.35	66.64	1.22	66.36	1.16	74.67	1.35	60.33
33.0	0.97	75.86	0.87	73.41	0.83	80.67	0.97	67.21
20.0	0.67	81.75	0.6	80.45	0.57	86.67	0.67	73.77
9.2	0.45	89.59	0.40	87.05	0.38	92.22	0.45	82.62
3.5	0.32	92.52	0.29	93.64	0.27	95.56	0.32	91.80
0.0	0.00	100.00	0.00	100.00	0.00	100.00	0.00	100.00

[a]Per cent bound water = $\frac{T-E}{T} \times 100$ where T=moisture at 100 per cent relative humidity, and E=moisture content in any other humidity.

Figure 7 shows that 60 per cent of the capillary bound water in lignite is retained as follows: (1) at 20° C. capillaries less than 1.75mμ in radius; (2) at 40° C. in capillaries less than 1.71mμ in radius; (3) at 50° C. in capillaries less than 2.45mμ in radius; and (4) in steam dried lignite at 20° C. in capillaries less than 1.40mμ in radius.

The Physical Structure of Lignite.

The Formation of Lignite.

It is now almost universally admitted that coal is a product of the metamorphism of vegetation and that lignite is one of the earlier stages in the transformation. Thiessen (14), using a grinding method of obtaining thin sections, has made microscopic studies of North Dakota Lignite and found it to be made up largely of woody matter. More recently, Gauger and Iverson (4) have continued the work using Jeffrey's slicing method of thin sections. Their results agree with those of Thiessen.

Vapor pressure studies also indicate that the decay of wood plays an important part in the formation of lignite. The work of Pidgeon and Maass (11), of McKenzie (9), of Larian (6), and that presented in this thesis on the vapor pressure of wood has agreed so strikingly with the results obtained by Porter and Ralston (12) on low rank coals, by Lavine and Gauger (7) on Dakota lignite and by Larian (6) on Minnesota peat that there is little doubt as to the validity of the wood to low-rank coal theory.

Thiessen (14) summarizes the present theory of lignite formation as follows:

"A large part of the study of peat formation is microbiolog-

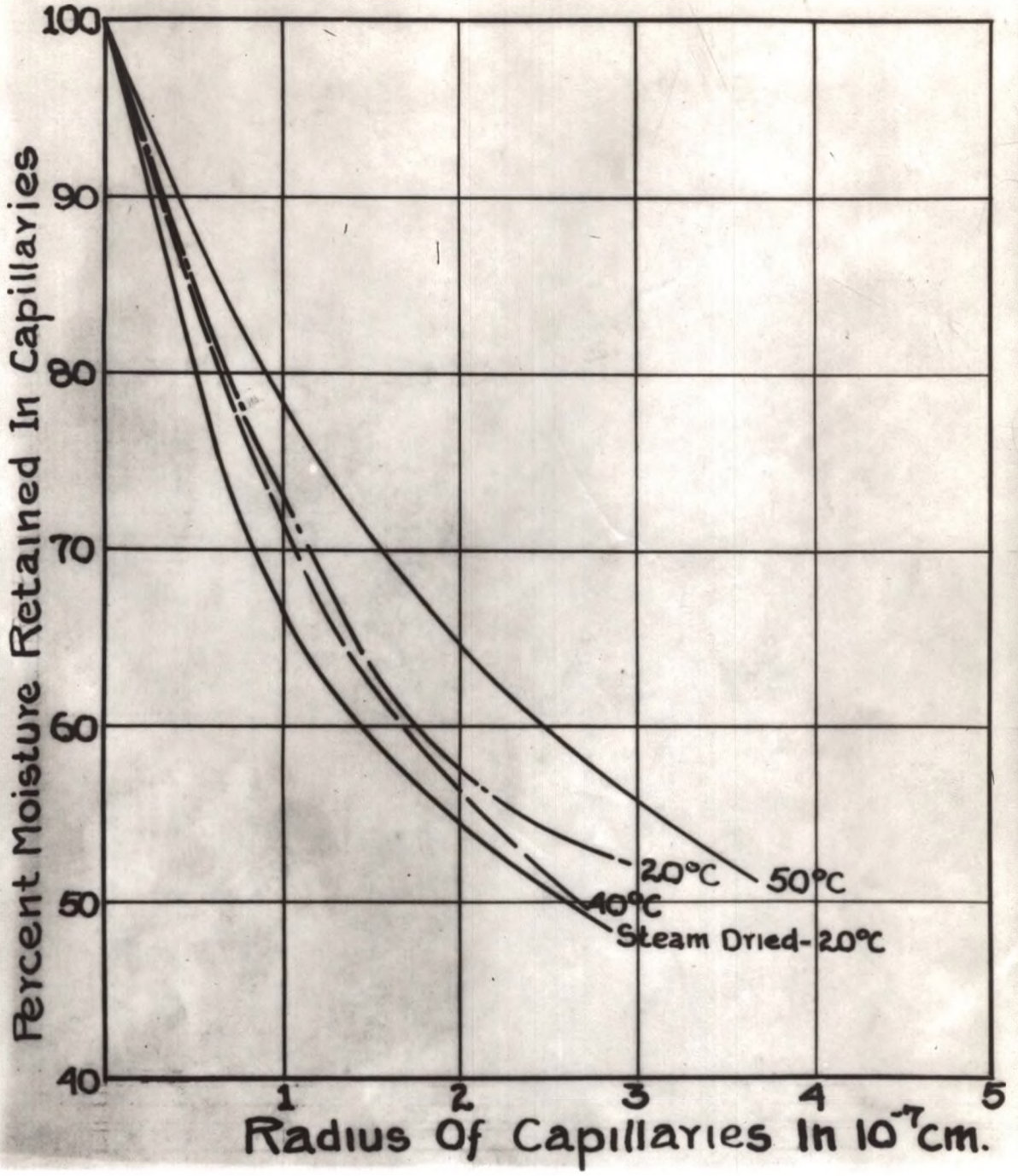

FIG. 7. MOISTURE – PORE SIZE

ical and chemistry of decay, in other words, rotting is the most important phase. It can roughly be divided into three phases: (1) decomposition entirely in the air; (2) decomposition in a zone, more or less fluctuating, between completely aerated zone and the zone of complete privation of air; and (3) complete submersion and privation of air. ----

"The first of these stages is by far the most important as in it the most important eliminating and the greatest changes take place through decay. Fungi are the initial and most important orgamisms. Bacteria follow the fungi. ----- In the semi-decomposed condition wood is further infested by actinomyces, flat worms, round worms, and all kinds of insect larvae and burrowing insects, as well as crust ceae. All of these organisms combined bring about the advanced stage of decomposition, disintegration, and comminution as it is generally found in any peat deposit. By the time this debris is covered up by debris subsequently formed only the smaller part is in the shape of fragments of rotten wood; the larger part is in the form of an attritus.

"As the debris is covered up more and more the moisture becomes greater and greater, up to the time when complete immersion ensues, the nature of the decomposing agencies changes. Fungi cease to exist completely. Actinomyces become rare, so do insects and other organisms. Bacteria are now both aerobic and facultative anaerobic. Disintegration and decomposition are materially slowed up. .....

"Where finally the debris, together with the roots and unmacerated stems is more deeply buried or submerged under a very

wet layer of peat, all life except that of the anaerobic bacteria has disappeared. ..... "

As the pressure becomes increasingly great, water is expelled from the attritus until the moisture content has been reduced from over eighty per cent to about forty per cent. The volume of the mass is materially reduced, its density increased. The color has become dark brown or black. The product is lignite, which may be considered as consisting in part at least of a hydrogel in which the water is contained in pores of varying size.

The Effect of Temperature and Pressure on the Physical Structure. Certain conclusions may be drawn now in regard to the effect of temperature and pressure on the physical structure of lignite. Figure 6 shows that heat treatment causes a collapse of capillaries of all size. Increasing the temperature from 20° to 40° C. the effect is small and the distribution of destroyed pores is in proportion to their occurrence in the original sample. Increasing the temperature to 50° C., however, causes the collapse of an increased number of the smaller capillaries as manifest by the fact that 60 per cent of the bound water is held at this temperature in capillaries whose average radius is greater than that at 20° C. or 40° C., for a corresponding quantity of water. A similar comparison shows that steam drying affects, in the main, the larger capillaries.

When lignite is heated in an atmosphere of saturated steam at elevated pressures its structure is definitely modified. The elimination of hysteresis with this material indicates that steam drying causes the hydrogel structure to "set" with the result that the further removal of moisture from this lignite is not accompan-

ied by shrinkage. In the case of freshly mined lignite heated at 50° C., the structure is modified but not set and the further dehydration of this material is accompanied by shrinkage which is responsible largely for hysteresis.

The Relation of the Moisture in Lignite to its Physical Structure. The results of the above experiments indicate that the moisture in lignite must be considered as part of its physical structure. The removal of this moisture by ordinary means involves a destruction of the lump form and inflicts, thereby, a severe disadvantage in the use of this fuel.

Various methods for the successful dehydration of lignite have been studied at this labotatory during the past few years. From theoretical considerations this should be accomplished by either of the following two methods:

1. By slowing down the rate of evaporation of moisture from the surface of the lump. This allows a very gradual removal of the moisture and disintegration should be a minimum.

2. By increasing the rate of transfer of moisture to the surface.

The steam drying method seems to fulfill the conditions required in the second case. An added influence in making this process successful with Dakota lignite is the change in the colloidal structure that is effected.

The first process can be accomplished by controlling accurately the humidity of the drying medium. This method has been investigated recently in this laboratory by the author with North Dakota lignite and the results are of particular interest in connection

with the question of the relation of the water in lignite to its physical structure.

A Carrier humidity drier which allowed careful control of the humidity and temperature of the air was used in this investigation. The procedure consisted in drying lumps of freshly mined lignite at a constant temperature and humidity for a definite period of time and then gradually decreasing the humidity while the dry bulb temperature remained constant. The humidity at the start of an experiment was above 90 per cent and was decreased only after sufficient time had been allowed for the lumps to reach equilibrium. The time required to reach equilibrium in a given atmosphere was determined by weighing a lump of lignite from time to time until constant weight had been reached. The weighing of the lump was facilitated by placing a balance on the dryer. A rod was attached to the right pan of the balance and this extended through a small opening in the top of the dryer into the drying zone proper. The lump of lignite was placed in a copper gauze basket which was attached to this rod. Weighings were made easily without any interruptions and without changing any of the conditions of the drying atmosphere. When this lump had dried to constant weight it was assured that the other lumps of lignite had reached equilibrium also.

Figure 8 shows the set-up used in this investigation.

The physical appearance of the lumps during the drying process was observed through a glass door in the dryer. A further indication of the physical strength of the dried coal was obtained from drop tests performed with ten pound samples of the fuel before

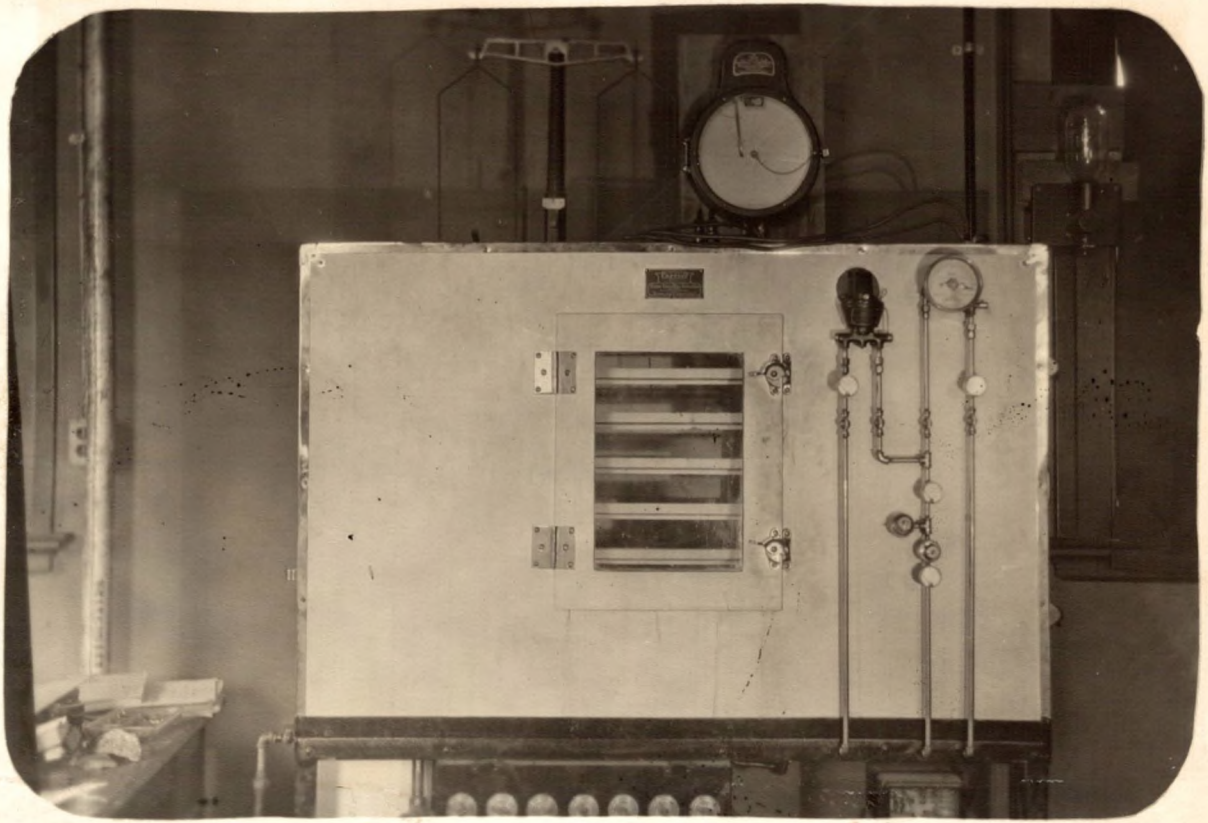

Fig. 8. Controlled Humidity Drier.

and after each experiment. This test consists in dropping the lignite from a height of seven feet on to a concrete floor. The cycle is performed 5 times after which the coal is sized and weighed. The ratio of the per cent retained on a 1½ inch screen for the dried and freshly mined lignite can be taken then as an index of the physical strength of the product.

Results of Humidity Drying of Lignite. A large number of experiments were performed during the course of this study. The results in every case were negative, that is, a good product was not obtained. Moreover, it was found that degradation accompanied the drying regardless of the rate at which the humidity was reduced. It was noticed also that slacking started shortly after the humidity had been reduced to 90 per cent and from that point the degradation of the lump was accelerated.

Table 8 gives data for a representative experiment in this study.

The method of humidity drying has been successfully utilized in the preparation of wood. According to Goss (5) the shrinkage of wood from the green state to the dry state varies from 5.1 to 12.6 per cent in the tangential direction; 2.2 to 7.6 per cent in the radial direction; and 0.1 to 0.3 per cent in the longitudinal direction. Although shrinkage is different in each of the three planes, it is uniform in any one of these planes. It is because of this latter fact that wood may be dried successfully by this method.

Table 8.

Controlled Humidity Drying of Lignite.

Time of drying hours		Humidity Data			Remarks
Hours at given humidity	Total	Dry bulb °F.	Wet bulb °F.	Relative Humidity %	
11.75		104	101.5	92	
10.25	22.00	104	100.5	90	Checking parallel to the bedding plane started.
7.00	29.00	104	99.5	87	Checking clearly evident.
6.75	35.75	104	98.0	82	The material was badly checked.
12.00	47.75	104	97.0	80	
10.00	57.75	104	95.5	74	
15.25	73.00	104	93.5	67	
5.00	78.00	104	91.0	60	

Drop Test Results.

	2"-lumps %	3"-lumps %	4"-lumps %
Per cent retained on 1½ in. screen - raw lignite	88.0	82.6	81.7
" " " on 1½ in. screen - dried lignite	10.5	24.4	17.9
Index	0.124	0.294	0.219
Index for steam dried lignite	0.400	0.450	0.423

The Successful Drying of Lignite.

Evidence obtained from microstructure studies indicates that in the transformation of wood to lignite there occurs more or less destruction of the tracheids and middle lamellae of the original wood substance. The coalification process also involved some destruction of the cementing material in the cell walls of the

woody substance. At the same time uneven deposition of the original plant material as well as disturbances during the coalification process causes an irregularity in the physical integration of the lignite. In wood the cells are built up in regular order and are definitely oriented throughout. In lignite the orientation is lost and the arrangement is chaotic. As a result when moisture is lost from lignite uneven shrinkage takes place in each of the three planes and the unequal forces so set up are sufficient to cause disintegration of the lump material. On the basis of this theory, the successful drying of lignite without disintegration should be possible only when the physical structure of the material is altered in a way as to prevent uneven shrinkage in any one plane. Controlled humidity drying should prove successful with lignite if the temperature of the drying medium is sufficiently high to cause a modification of the structure as outlined above.

Steam drying of Dakota lignite by the Fleissner process as performed by Lavine (8) has quite successfully coped with this problem. It has been shown that the hydration of Dakota lignite is not the reverse process of dehydration. A certain amount of hysteresis is evidenced. As the temperature increases the region of hysteresis decreases. With steam dried lignite it disappears almost entirely. As the temperature rises progressively the dehydration isotherms are continuously shifted to a region of lower moisture content. This means that there is a destruction of capillaries. An inspection of Figure 7 and Table 7 shows that it is the larger capillaries which undergo the greatest destruction in steam dried lignite. This phenomenon was not observed in any of the other experiments.

A mechanism of the processing of lignite with saturated steam suggests itself. A destruction of capillaries of all sizes goes on, the larger suffering to the greater extent. The hydrogel is set so that no further changes in structure take place at ordinary temperatures. The action of saturated steam is such that the thermal expansion and shrinkage must be so modified that the difference of these properties in the different directions does not cause disintegration. This property is probably a function of the setting.

Summary.

1. The following water vapor sorption isotherms have been studied:

   (1) Woods at 20° C.

   (2) Freshly mined lignite at 50° C.

   (3) Steam-dried lignite at 20° C., processed at pressures varying from 5 to 15 atmospheres.

   (4) Air-dried lignite at 20° C.

2. Increased temperature decreases the hysteresis area. In steam-dried lignite hysteresis is practically eliminated.

3. The phenomenon of hysteresis has been discussed in detail.

4. Low temperature drying of lignite by controlled humidity has proven unsuccessful.

5. A mechanism for the successful drying of lignite has been advanced.

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Acknowledgement.

The writer wishes to acknowledge his indebtedness to Professor L. C. Harrington, Dr. Irvin Lavine, and Dr. A. W. Gauger for their direction and interest in his work. The writer further wishes to acknowledge his indebtedness to Mr. Ben Berger for his kindness in granting the Berger Fellowship.